10-1957

Annotated bilbiography of alpha, beta, gamma, delta-tetraphenylporphine

Charles V. Banks
Iowa State College

Samuel Anderson
Iowa State College

Annotated bilbiography of alpha, beta, gamma, delta-tetraphenylporphine

Abstract
This annotated bibliography on alpha, beta, gamma, delta-tetraphenylporphine has been prepared as a reference for analytiical research. The authors hope that this bibliography will be of service to those engaged in research and development work and that further work on the analytical applications of this interesting reagent may be encouraged by the availability of this reference.,

Disciplines
Chemistry

Chemistry-General (UC-4)

UNCLASSIFIED

ISC-921

UNITED STATES ATOMIC ENERGY COMMISSION

RESEARCH AND DEVELOPMENT REPORT

ANNOTATED BIBLIOGRAPHY OF ALPHA, BETA, GAMMA, DELTA-TETRAPHENYLPORPHINE

by

Charles V. Banks and Samuel Anderson

October, 1957

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
Contract W-7405 eng-82

UNCLASSIFIED

ISC-921

This report is distributed according to the category Chemistry-General, as listed in TID-4500, February 15, 1958.

Legal Notice

Printed in USA. Price 50 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

ANNOTATED BIBLIOGRAPHY OF ALPHA, BETA, GAMMA, DELTA-TETRAPHENYLPORPHINE

by
Charles V. Banks and Samuel Anderson

Introduction

This annotated bibliography on alpha, beta, gamma, delta-tetraphenylporphine has been prepared as a reference for analytical research. The authors hope that this bibliography will be of service to those engaged in research and development work and that further work on the analytical applications of this interesting reagent may be encouraged by the availability of this reference.

The references in this bibliography deal with the methods of preparation and purification of alpha, beta, gamma, delta-tetraphenylporphine, the properties of some of its metal complex salts, and its analytical applications. The references are listed chronologically.

1936

1. Albers, V. M. and Knorr, H. V., "Spectroscopic Studies of the Simpler Porphyrins. I. The Absorption Spectra of Porphine, ms-Methyl Porphin, ms-Ethyl Porphin, ms-Propyl Porphine, and ms-Phenyl Porphin," J. Chem. Phys., 4, 422 (1936) [C. A., 30, 5884 (9) (1936)].

   The molecular absorption coefficients of porphin and four ms-substituted porphines have been measured throughout the visible region, and the curves showing absorption coefficient as a function of wave length are shown. All of the substances have a very strong absorption band at the violet end of the visible region. The rest of the spectrum, while similar in pattern for all the substances, shows some characteristic differences.

1938

2. Rothemund, Paul, "Chemiluminescence of the Chlorophylls and of Some Other Porphyrin Metal Complex Salts," J. Am. Chem. Soc., 60, 2005 (1938) [C. A., 32, 7492 (7) (1938)]

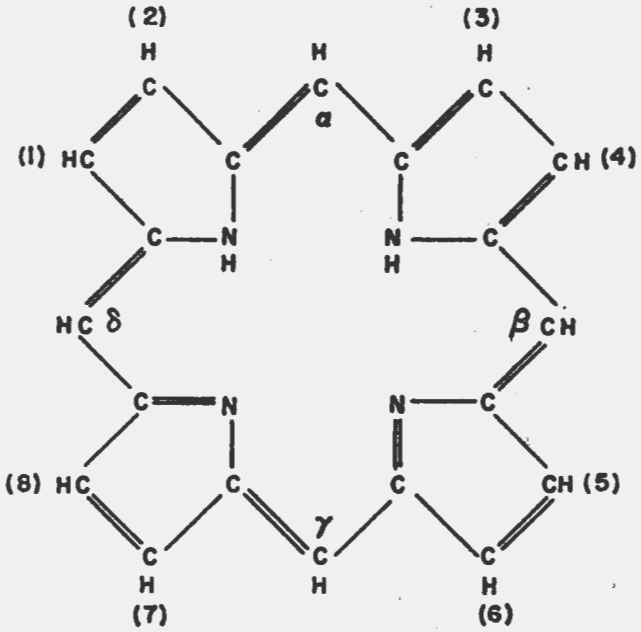
Chlorophyll a or b is added to tetralin and heated to 125°. A red chemiluminescence is just perceptible; increasing the temperature increases the intensity, exhibiting a red glow at 160 to 1900°, then disappears when soln. is boiled for a few minutes. Addition of more chlorophyll to the hot soln. causes chemiluminescence to reappear. The Mg and Zn complex salts of porphine and α, β, γ, δ -tetraphenylporphine react in the same manner and give the same color. The free porphines and α, β, γ, δ -tetraphenylporphine or their hemins, Cu, Ni, Co, or Ag complex salts give a negative reaction. When Mg is added to a solution of α, β, γ, δ -tetraphenylporphin in tetralin and allowed to stand for some time, the chemiluminescence can be observed upon bubbling O_2 or CO_2 through the hot soln. Xylene, P-cymene or bromo-cyclohexane may be used as solvents for porphyrin, Mg, or Zn complex salts. After the reaction the soln. differs spectroscopically from the unheated soln.

1939

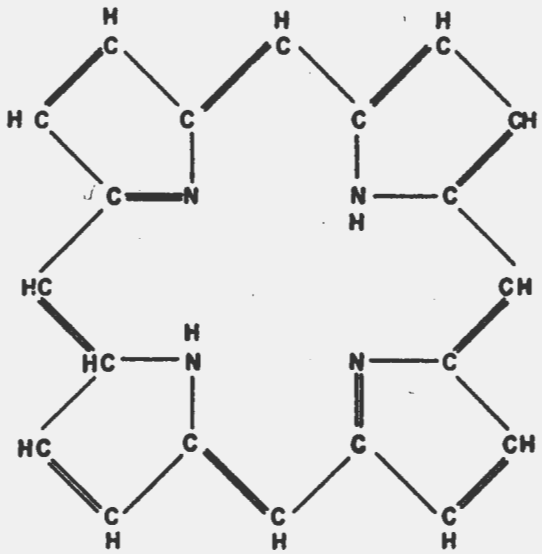
3. Rothermund, Paul, "The Structure of the Porphine Ring System," J. Am. Chem. Soc., 61, 2912-15 (1939); cf. C. A., 30, 3833 (3) [C. A., 34, 440 (1) (1940)].

In the prepn. of porphin from pyrrole and formaldehyde the reaction mixture contained in addition to porphin, a porphyrin with a hydrochloric acid number lower than that of porphin. In comparison with porphin the two main absorption bands of this porphyrin were shifted about 100 A° toward the red region of the spectrum. The new porphyrin is formed only in small quantities; its HCl No. was 0.5 while porphine, the main product had an HCl No. of 3.3. The elementary analyses checked with each other within exptl. errors. Each formed complex salts with Mg, Fe and Cu. The new porphyrin was given the name isoporphine. One absolute configuration cannot be assigned to either compound.

α, β, γ, δ-Tetraphenylporphine was synthesized and shown to consist of two isomers, mp 350°, 13.5 and 6.5.



PORPHINE



ISOPORPHINE

1940

4. Albers, V. M. and Knorr, H. V., "The Absorption Spectra of α, β, γ, δ-Tetraphenylporphine and a Series of its Metal Complex Salts," Phys. Rev., 57, 346 (1940) [C. A., 35, 4685 (6) (1941)].

The absorption spectra of α, β, γ, δ-tetraphenylporphine and the Cd, Ag, Zn, Pb, Ni, Co, FeCl, MnCl and $SnCl_2$ complex salts have been studied over the region from 900 mu to 370 mu in benzene solution, using a recording spectroradiometer. There were no absorption bands observed in any of these substances between 900 mu and 700 mu. All, however, showed characteristic absorption in the visible region. Absorption curves, showing molecular absorption coefficients as a function of wave length have been determined for all these substances from 700 mu to 370 mu.

5. Albers, V. M., and Knorr, H. V., "The Fluorescence Spectra of α, β, γ, δ-Tetraphenylporphine and Some of its Metal Complex Salts," Phys. Rev., 57, 347 (1940) [C. A., 35, 4685 (7) (1941)].

The fluorescence spectrum of α, β, γ, δ-tetraphenylporphine in anhydrous benzene and under an atmosphere of nitrogen, has been photographed. The spectra of the Ni, FeCl, and Ag complex salts have also been photographed under similar conditions. A fluorescence band was observed with its maximum at 655 mu for each of these substances. This same band is also observed for tetraphenylporphine under an atmosphere of carbon dioxide. Two additional bands have also been observed in the near infra-red for tetraphenylporphine.

1941

6. Rothermund, Paul and Menotti, Amel R., "The Synthesis of α, β, γ, δ-Tetraphenylporphine, J. Am. Chem. Soc., 63, 267-70 (1941) cf. C. A., 34, 438 (8) [C. A., 35, 1408 (8) (1941)].

Heating 10 ml of pyrrole, 20 ml of benzaldehyde and 20 ml of pyridine in a nitrogen atm in special Carius tubes at 220°C for 48 hrs gives 1.7 - 2 gm of α, β, γ, δ-tetraphenylporphine, bluish-red needles, M. P. 450°C; HCl No. 13.5; the solubility is 35 mg/100 ml in glacial AcOH and approx. 250 mg in 100 ml 90% HCO_2H. Its acid solutions are bright green and exhibit a characteristic acid porphyrin spectrum; solutions in other solvents are magenta-red with red fluorescence. In HCl, it gives an amorphous HCl salt of indefinite compn.; it decomposes slowly on standing and rapidly in the presence of moisture. The absorption spectra of α, β, γ, δ-tetraphenylporphine in ether, $CHCl_3$, C_5H_5N, $CHCl_3$-HCl, AcOH and 21% HCl are given. In its prep. an isomer is formed. (HCL No. 8.5)

7. Albers, V. M. and Knorr, H. V., "Spectroscopic Studies of the Simpler Porphyrins. III. The Absorption Spectra of ms-Tetraphenylporphine and a Series of its Metal Complex Salts," J. Chem. Phys., 9, 497-502 (1941); cf. C. A., 35, 3169 (9), 4685 (6) [C. A., 35, 6186 (7) (1941)].

The molar absorption coefficients of ms-tetraphenylporphine and the Cu, Ag_2, Zn, Cd, Hg, $SnCl_2$, Pb, MnCl, FeCl, Co and Ni complex salts were measured (360 - 400 mu). Curves are shown.

1942

8. Krimler, D., "The Dipole Moment of ms-Tetraphenylporphine," J. Am. Chem. Soc., 64, 2993-4 (1942) [C. A., 37, 810 (1) (1943)].

The more abundant isomer of ms-tetraphenylporphine was found to have a polarization of 310 and an electronic polarization of 297. Measurements of polarization at different temperatures gave no indication of a decrease in polarization with increasing temperature. Both methods indicate that the compound has zero moment, although the data do not permit distinguishing between a moment of a few tenths and a zero moment.

1943

9. Aronoff, S. and Calvin, M., "The Porphyrin-Like Products of the Reaction of Pyrrole with Benzaldehyde," J. Org. Chem., 8, 205-23 (1943) [C. A., 37, 5068 (9) (1943)]

When 5 cc of pyrrole and 10 cc of pyridine are heated at 100°, 165°, 190°, 220° and 245° for from 5 days at the lowest temperature to 18 hours for the highest, up to 10% (48 hours at 190° to 220°) purple crystals of a porphyrin mixture of the compound $C_{44}H_{30}N_4$ (α, β, γ, δ-tetraphenylporphine) are obtained. The mixture is fractionated chromatographically using talc as absorbent and Cl_2:CHCl as solvent.

1944

10. Calvin, M., Ball, R. H. and Aronoff, S., "α, β, γ, δ-Tetraphenylchlorine," J. Am. Chem. Soc., 65, 2259 (1943), cf. C. A., 37, 5068 (9) [C. A., 38, 95 (8) (1944)].

In the prepn. of tetraphenylporphine from pyrrole and benzaldehyde (cf. Rothemund, C. A., 34, 439 (8), the spectra of the resulting compounds indicated that the 1st two most abundant products might be related as porphyrin to chlorine. It is shown that these products are related by oxidation and reduction and thus the next most abundant product is considered to be tetraphenylchlorine.

1947

11. Ball, R. H., Dorough, G. D., and Calvin, M. (Univ. of Calif., Berkeley), "Further Study of the Porphine-Like Products of the Reaction of Benzaldehyde and Pyrrole," J. Am. Chem. Soc., 68, 2278-81 (1946); cf. C. A., 38, 95 (8) [C. A., 41, 752e (1947)].

The main products from 5 cc pyrrole and 10 cc each of benzaldehyde and pyridine are α, β, γ, δ-tetraphenylporphine, $C_{44}H_{30}N_4$, and α, β, γ, δ-tetraphenylchlorin, $C_{44}H_{32}N_4$. The yield of the latter is better at higher temps. (4% at 170°, 12% at 200°, and 20 to 5% at 220°). The

addn. of 5 gm of $Zn(OAc)_2$ to the reaction mix. increases yield from 4-5 to 10-11% (based on pyrrole); the product in this case is the Zn complex of α, β, γ, δ - tetraphenylporphine which upon treatment with 6N HCl yields practically pure α, β, γ, δ -tetraphenylporphine. The tetraphenylporphine and the tetraphenylchlorin can be sepd. by chromatography on talc from $ClCH:CCl_2$ (max. of 9 mg/sq cm of cross sect. area of column). The Cu salt of the tetraphenylchlorin is oxidized to that of the tetraphenylporphine by a mole of O. The Zn salt of the tetraphenylporphine can be reduced by Na in ethanol to that of the tetraphenylchlorin. Hydrogenation of the tetraphenylporphine gives the tetraphenylchlorin. These reactions are not complete and their course is followed by absorption curves. The structures of the tetraphenylporphine and the chlorin are confirmed by direct analysis.

1948

12. Calvin, M. and Dorough, G. D., "Possibility of a Triplet State Intermediate in the Photo-Oxidation of a Chlorin," J. Am. Chem. Soc., 70, 699-706 (1948) [C. A., 42 3675e (1948)].

When the Zn salt of tetraphenylchlorin was allowed to stand for a few hours the green color of the solution, which gave a red fluorescence, changed to a yellow colored solution with no fluorescence. An absorption spectrum of such a solution showed the Zn chlorin band still existing at 6200 A°, the formation of a Zn chlorin band at 5500 A°, also the formation of some new substance with a high absorption in the region 4650 A°. The degradation was found to be caused by a light induced oxidation by molecular oxygen. Other oxidizing agents gave the same result. Ortho and para quinones in a deoxygenated benzene solution was found to give a quantitative yeild of only one product, Zn tetraphenylporphine.

13. Rothemund, P., and Menotti, R. (Ohio State Univ., Columbus). "Porphyrin Studies. V. "The Metal Complex Salts of α, β, γ, δ -Tetraphenylporphine," J. Am. Chem. Soc., 70, 1808-12 (1948); cf. C. A., 35, 1408 (8) [C. A., 42, 6357 (1948)].

Salts of α, β, γ, δ -tetraphenylporphine are prepd. in AcOH or HCO_2H with the acetate of the metal, in hot C_5H_5N, or in 40% MeOH-KOH. In the formulas, R = $C_{44}H_{28}N_4$. The salts analyzed are RCu, RHAg, RAg_2, RAu_2Cl_4, RMg, RH_2MgO, RZn ($C_{44}H_{28}N_4Zn$ given), RCd·C_5H_5N (?, original gives $C_{44}H_{28}Cd \cdot C_5H_5N$), RCd, RHg, RTl, $RSnCl_2$, RPb C_5H_5N, RMnCl, RFeCl, RCO, and RNi; qualitative and solubility data are given. Absorption max. are given for the above salts and also Li, Na, K and Rb. The salts have high surface luster, show selective adsorption in the visible region of the spectrum and melt from 400 to 500°; all except MnCl and Au_2Cl_4 salts sublime from 400 to 450° with partial decompn. of complex. The K and Tl complexes decompn. in C_6H_6 or ether; the Mg, Hg and Pb complexes split when shaken with 50% AcOH; the Zn and Ag complexes are stable in 50% AcOH but decompn. slowly in HCl; the other salts are stable to concd. HCL on the steam bath. The complexes of Li, Na, K, Rb, and Ce decompn. rapidly when exposed to strong light; the Mg and Tl compds. showed spectrum shifts under these conditions. The Zn, Mg and Cd salts showed a bright red chemiluminescence when heated above 125° in tetralin, xylene, p-cymene, or bromocyclohexane. When freshly distilled tetralin is used, only a faint glow of short duration is observed; on adding a few drops of tetralin which has been standing for some time, the bright red glow reappeared.

1949

14. Huennekens, F. M., and Calvin, M. (Univ. of Calif., Berkeley) "Photochemical Studies of the Porphyrins. II. "The Photoxidation of Chlorins by Various Quinones," J. Am. Chem. Soc., 71, 4024-31 (1949); cf. C. A., 42, 3675e [C. A., 44, 2855e (1950)].

The Zn and Mg complexes of tetraphenylchlorin can be photooxidized to the corresponding porphines by ortho and para-quinones. Plotting of the quantum number against the standard oxidation potential yields one straight line for the o-quinones and another straight line for the p-quinones. The rate of the Zn chlorin reaction is faster than the Mg by a factor of almost 8.

15. Huennekens, F. M., and Calvin, M. (Univ. of Calif., Berkeley), III. "The Photooxidation of Chlorins by by Oxygen," J. Am. Chem. Soc., 71, 4031-5 (1949) [C. A., 44, 2856a (1950)].

Zinc and magnesium tetraphenylchlorins can be photooxidized by oxygen to the corresponding porphine. A secondary reaction occurs between H_2O_2 and the porphin, yielding a product similar to that obtained by "bleaching" chlorophyll in the presence of O_2.

1950

16. Barnes, J. W. and Dorough, G. D., "Exchange and Replacement Reactions of α, β, γ, δ -Tetraphenylporphines," J. Am. Chem. Soc., 72, 4045-50 (1950) [C. A., 45, 5680e (1951)]

The metalloporphines derived from the smaller bivalent metals are in general quite resistant to hydrolysis. Replacement reactions, however, are possible as shown by conversion of the Zn salt into the Cu salt by prolonged heating with cupric acetate. The smaller bivalent metalloporphines also have similar spectra. The spectra of the large bivalent metalloporphines differ from the smaller bivalent metals and undergo replacement reactions as follows: Pb or Hg in a metalloporphine is replaced quantitatively by a smaller bivalent metal such as Zn or Cu and the larger Pb ion is replaced by a Hg ion. Even with a large excess of inorganic metal ion the reaction does not go in the reverse direction. The porphine salts of the alkali metals are readily hydrolyzed by H_2O, and exhibit a spectra in the case of α, β, γ, δ - tetraphenylporphine similar to Pb and Hg, and undergo replacement reactions as follows: The alkali metal ions in an alkali metalloporphine are rapidly and completely replaced by a smaller bivalent ion, a large bivalent ion,

or a smaller alkali metal ion. None of these reactions proceed in the reverse direction even in an excess of inorganic metal ion. Complete equilibrium of the activity in a pyridine solution of NaI and di-Na tetraphenylporphine is observed at room temp. in less than 6 minutes.

1951

17. Dorough, G. D., Miller, J. R., and Huennekens, F. M. (Washington Univ., St. Louis), "Spectra of the Metallic Derivatives of α, β, γ, δ -Tetraphenylporphine," J. Am. Chem. Soc., 73, 4315-20 (1951); cf C. A., 41, 752d [C. A. 46, 5968b (1952)].

The absorption spectra of 17 different metallo derivatives of α, β, γ, δ -tetraphenylporphine are correlated with the nature of the bonding between the central metal constituent and the N atoms on the porphine ring. Methods of preparation and details of certain chemical properties of the metallophenylporphines are described; phosphorescence, fluorescence, and absorption spectra of the tetraphenylporphine compounds are given.

1952

18. Dorough, G. D. and Huennekens, F. M. (Univ. of Calif., Berkeley), "The Spectra of α, β, γ, δ -Tetraphenylchlorine and its Metallo Derivatives," J. Am. Chem. Soc., 74, 3974-6 (1952); cf. C. A., 46, 5968a [C. A., 47, 4873g (1953)].

The absorption spectra of α, β, γ, δ -tetraphenylchlorine and some of its metallo complex derivatives are given. A method is given for the separation of α, β, γ, δ -tetraphenylchlorine (I) and α, β, γ, δ -tetraphenylporphine (II); to a mixture (400 mg of (I) and (II) free bases prepared by heating benzaldehyde, pyrrole, and pyridine in a sealed tube 36-38 hrs. at 200 to 220°) in the min. atm. of C_2HCl_3, was added 1 gm zinc acetate, and the mixt. heated gently (the course of the reaction was followed visually with a spectroscope) until all of the (II)

was converted to the Zn derivative, then absorbed on a talc column and developed with $Cl_2C{:}CHCl$; the Zn derivative of (II) passed through quickly, leaving on the column the free (I) which was eluted with acetone, 20 cc C_2HCl_3 added to the eluant, the resulting soln. washed with H_2O, treated with 25 cc 8N HCl, neutralized with 6N NH_4OH, washed again several times with H_2O, dried with Na_2SO_4, and chromatographed again to give a high purity of (I). All metal derivatives of (I) are unstable to light induced oxidations by molecular oxygen, some are even unstable in the solid state.

19. Dorough, G. D. and Miller, J. R. (Washington Univ., St. Louis), "Pyridinate Complexes of Some Metallo-derivatives of Tetraphenylporphine and Tetraphenyl-chlorine," J. Am. Chem. Soc., 74, 3477-81 (1952), cf. C. A., 47, 4873g (1953) [C. A., 47, 4874 (1953)].

The complex formation of the Mg, Zn, Cd, Hg and Cu II derivatives of α, β, γ, δ -tetraphenylporphine (I) and α, β, γ, δ -tetraphenylchlorine (II) with pyridine was investigated by determining the optical density of any wave length at which the complexed and uncomplexed derivatives differed appreciably. The Mg derivatives of (I) and (II) formed dipyridinates, whereas all other metal derivatives formed monopyridinates. The equilibrium constants, ΔH cal/mole, and the standard entropy changes, which were all negative, were determined in all cases. The absorption spectra of each complex of (I) and (II) were run in C_6H_6 and pyridine or a mixture of the two. The Co(III) derivative of (I) chloride monopyridinate is not appreciably dissociated at a concentration of 4×10^{-5} M, which corresponds to an association constant of greater 10^7. The Cu(II) derivative of (I) forms a monopyridinate with an association constant at 30°C of about 0.05, similar to that of the Ni(II) derivative, whereas the Ag(II) derivative is a much weaker Lewis acid toward pyridine.

1953

20. Seely, Gilbert Randall, "Photochemistry of Porphyrins," (Univ. of Calif., Berkeley), U. S. Atomic Energy Commission, Report No. UCRL-2417, 120 pp (1953) [C. A., 48, 11196h (1954)].

This paper is about the reduction of Zn tetraphenylporphine by a series of ene-diol and related compounds. The reduction products were identified as Zn tetraphenylchlorine (dihydroporphine) and Zn tetrahydrotetraphenylporphine. The spectrum of the latter was established. The reduction was carried out in the presence of light. Some of the reducing agents were benzoin, p-dimethylaminobenzoin, ascorbic acid, dihydroxyacetone, reductone and dihydroxymaleic acid. The kinetics of the fastest reaction, benzoin, was studied. The reaction rate was directly proportional to the light absorbed by the benzoin but dependent on the light absorbed by Zn tetraphenylporphine. The photo-oxidation of Zn tetrahydrotetraphenylporphine to Zn tetraphenylporphine was also studied. The nature of the metal in the center of the porphyrin ring was correlated with the fluorescence, magnetic susceptibility, and the stability of the metal porphyrin complex.

21. Linschitz, Henry and Abrahamson, E. W. (Syracuse Univ.) "Kinetics of Porphyrin-Catalyzed Chemiluminescent Decomposition of Peroxides, and Mechanism of Photosensitized Oxidation," Nature, 172, 909-10 (1953), cf. C. A., 32, 7344 (7) [C. A., 48, 4313f (1954)].

Metallic complexes of phthalocyanine dyes function as catalase models for the decomposition of peroxides. In hot hydrocarbon solvents, a bright chemiluminescence accompanies these decompositions. The decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide(I) by Zn tetraphenylporphine(II) in tert-butylbenzene at 149° was studied. It was found that (1) initial increase in rate of (I) (over uncatalyzed (I) is proportional to initial concentration of (II); (2) $d(II)/dt = k_o(II)(I)$, where $k_o = 0.5 \pm 0.1$ l. $mole^{-1}$ min^{-1}; (3) the turn-over No. was 20-30 mol. of I per mole of II; (4) luminescence intensity = k (I) (II); (5) reaction products were found to be 3,4-dihydro-1-(2H)-naphthalenone and water; (6) with II as catalyst, cumene hydroperoxide and ter-butyl peroxide gave only feeble emission; di-tert-butyl peroxide gave no emission.

1954

22. Priesthoff, J. H. and Banks, C. V. (Iowa State College, Ames), "A New Method of Purifying α, β, γ, δ -Tetraphenylporphine," J. Am. Chem. Soc., 76, 937-8 (1954) [C. A., 49, 10318 (1955)].

The tarry product from the reaction of pyrrole and benzaldehyde and zinc acetate in pyridine was extracted with acetone and crystalline Zn tetraphenylporphine obtained. It was found that about 5 gm of the complex was lost for each liter of acetone. The new method depended upon decomposing the complex with acid and chromatographing the free base tar solution on Al_2O_3. The free base-eluate was chromatographed on Magnesol to yield pure tetraphenylporphine.

23. Shibata, K., Benson, A. A. and Calvin, M. (Univ. of Calif., Berkeley), "Absorption Spectra of Suspensions of Living Microorganisms", Boichim. et Biophys. Acta, 15, 461-70 (1954) [C. A., 49 5564f (1955)].

Besides the spectra of microorganisms, the spectrum of Zn tetraphenylporphine in the powdered form was also obtained and the curves compared with those obtained in solution. The technique consisted of providing the sample and blank cell compartments, on the sides of light transmission, with identical opalescent plates which uniformly diffuse all of the light as it leaves the cuvets.

1955

24. Dorough, G. D. and Miller, J. R. (Washington Univ., St. Louis), "Fundamental Properties of Porphyrin-Ring Systems. VI. An Attempted Preparation of a Simple Tetrahydroporphine," J. Am. Chem. Soc., 74, 6106-8 (1952); cf. C. A., 47, 4874a [C. A., 49, 1699 (1955)].

In the conversion of tetraphenylchlorine(I) to tetraphenyl-tetrahydroporphine(II) by catalytic hydrogenation, two compounds (III) and (IV) were isolated from the reaction. (I) (100 cc, 2 x 10^{-4} M in ether) stirred 30 min. under H at 1 atm. with 0.1 cc freshly prepared Raney Ni, the Ni filtered off, (I) removed from the

filtrate by 8-10 extractions with 100-cc portions of 5N HCl in a minimum of light, the ether solution washed with water, 6N NH_4OH and water, evaporated to dryness in vacuum, and the residue in a minimum of $Cl_2C{:}CHCl$ chromatographed on talc yielded 2-4% (III). (III) with EtMgI yields the Mg derivative. (IV) is formed in the above described reaction but the yield is improved if the reduction is carried out with 0.2 gm Raney Ni in 20 cc dioxane. (IV) is obtained in 2% yield contaminated with 5-10% (I). (III) is identified tentatively as tetrahydroporphine. (IV) may be a tetrahydroporphine with adjacent pyrroles reduced, but some of its properties are similar to those of a chlorin. Absorption spectra are presented and discussed.

25. Seely, Gilbert R., and Calvin, M. (Univ. of Calif., Berkeley), "Photochemical Studies of the Porphyrins III. Photoreduction of a Porphyrin by Benzoin," J. Chem. Phys., 23, 1068-78 (1955); cf. C. A., 44, 2855e.

The kinetics of the photoreduction of Zn tetraphenylporphine by benzoin was studied. The products were successively the dehydro(chlorin) derivative, a tetrahydro derivative, and possibly a hexahydro compound. The primary requirement is the photoactivation of benzpin; a secondary reaction, involving photoactivated porphyrin, was also demonstrated. The quantum yield based on light absorbed by benzoin varied between 0.01 and 0.06.

1956

26. Thomas, D. W. and Martell, A. E., "Tetraphenylporphine and Some Para-Substituted Derivatives," J. Am. Chem. Soc., 78, 1335 (1956).

This paper gives the method for synthesizing para-methyl, methoxy, chloro and nitro derivatives of tetraphenylporphine directly from pyrrole and the corresponding aldehyde. Chlorins and other by-products were separated chromatographically and characterized by spectrophotometric analysis. The yields of main product decrease as the acceptor activity of the aldehyde carbonyl increases.

27. Thomas, D. W. and Martell, A. E., "Absorption Spectra of Para-Substituted Tetraphenylporphines," J. Am. Chem. Soc., 78, 1338 (1956).

The absorption spectra of tetraphenylporphine, tetra-(p-methoxyphenyl)-porphine, tetra-p-tolyl porphine, tetra-(p-chlorphenyl)-porphine and tetra-(p-nitrophenyl)-porphine in the ultraviolet, visible and infrared regions are reported. The visible and ultraviolet spectra indicate that the para-substituent exert only a small effect on the electronic transitions of the porphine ring system. Assignments of infra-red frequencies are made where possible.

1957

28. Banks, C. V. and Bisque, R. E. (Iowa State College, Ames) "Spectrophotometric Determination of Zinc and other Metals with Alpha-, Beta-, Gamma-, Delta-Tetraphenylporphine." Anal. Chem., 29, 522 (1957).

The zinc complex salt of α, β, γ, δ -tetraphenylporphine has a strong absorption band at 551 mu. When zinc acetate is added to a solution of α, β, γ, δ -tetraphenylporphine in glacial acetic acid, the following equilibrium is established in 60 to 70 minutes at room temperature:

$$Zn^{++} + TPPH_2 = ZnTPP + 2H^+ .$$

The addition of an acetate salt functions as a base and shifts the equilibrium to the right. However, when the maximum amount of zinc present is complexed, addition of more acetate salt reverses the equilibrium. Curves are given showing absorbance versus ionic strength. A method is also given for indirect determinations of several other metals in certain compounds.